



# Graphene-wrapped Pt/TiO<sub>2</sub> photocatalysts with enhanced photogenerated charges separation and reactant adsorption for high selective photoreduction of CO<sub>2</sub> to CH<sub>4</sub>

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## ABSTRACT

Artificial photosynthesis efficiency for selective CO<sub>2</sub> conversion to CH<sub>4</sub> as chemical energy-rich molecule is dependent on the photogenerated charges separation and reactant adsorption property of photocatalyst. Here we report a novel fabrication of core-shell-structured photocatalysts of Pt/TiO<sub>2</sub>-nanocrystals wrapped by reduced graphene oxide (rGO) sheets ((Pt/TiO<sub>2</sub>)/rGO). The ultrafine anatase TiO<sub>2</sub> nanocrystals with coexposed {001} and {101} facets acted as the fountain of the photogenerated charges primitively. Pt nanoparticles (NPs) deposited on the TiO<sub>2</sub> nanocrystals can gather and transfer the stimulated electrons originated from anatase TiO<sub>2</sub> nanocrystals. The all-solid-state electron multiple transmission (EMT) system with TiO<sub>2</sub>-nanocrystal(core)-Pt (mediator)-rGO(shell) nanojunction is not only favorable to the vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO and enhance the separation efficiency of photogenerated electrons and holes, but also the surface residual hydroxyl and extended  $\pi$  bond of wrapping rGO sheets can improve the adsorption and activation capabilities for CO<sub>2</sub> reactant. (Pt/TiO<sub>2</sub>)/rGO ternary photocatalysts exhibit excellent performance for the multi-electron process of selective photocatalytic CO<sub>2</sub> conversion to CH<sub>4</sub>. Among the prepared catalysts, (Pt/TiO<sub>2</sub>)/rGO-2 catalyst shows the highest photocatalytic activity and selectivity for CO<sub>2</sub> conversion, i.e., the formation rate of CH<sub>4</sub> is 41.3  $\mu\text{mol g}^{-1} \text{h}^{-1}$  and the selectivity of CO<sub>2</sub> conversion to CH<sub>4</sub> product is 99.1%, and its apparent quantum efficiency for CH<sub>4</sub> product is 1.93%. As a heuristic the fabrication of core-shell structured (Pt/TiO<sub>2</sub>)/rGO photocatalysts will stimulate more novel ideas for application to light-chemical energy conversion.

## 1. Introduction

Global climate change caused by the rapid growth of carbon dioxide (CO<sub>2</sub>) concentrations in our atmosphere is regarded as one of the greatest crises in this century [1,2]. Scientists have long dreamed of mimicking photosynthesis of green plants, by using the energy in sunlight to knit together hydrocarbon fuels from water and CO<sub>2</sub>, the chief culprit in global warming [3,4]. Since the pioneering researches reported by Fujishima [5], a variety of high efficient semiconductor-based photocatalysts with the suitable band gap for CO<sub>2</sub> reduction with H<sub>2</sub>O have been reported [6–10]. However, practical applications of photocatalytic reduction of CO<sub>2</sub> are limited because of the low selectivity of reductive production and the low fuel-conversion efficiency caused by the rapid recombination of photogenerated electrons and holes. Therefore, the design and synthesis of efficient photocatalysts to

decrease the recombination of photogenerated charge carriers and/or enhancing the selectivity and activity of reduction products have attracted much attention in global [11,12].

Among the previous reported photocatalysts, TiO<sub>2</sub> is the most widely applied semiconductor materials because of its nontoxicity, long-term stability, corrosion resistant and cost inexpensive [13–17]. The catalytic activities of TiO<sub>2</sub>-based materials for photocatalysis are related to the exposed low-index facets of {001}, {010} and {101} with the average surface energies of 0.90, 0.53 and 0.44 J m<sup>-2</sup> in single anatase nanocrystals, respectively [18]. The role of {101} facet is the selective gathering of surface photogenerated electrons, while surface photogenerated holes remain on the surface of {001} facet, because of their different the electronic energy levels and the distribution of potential trapping sites [19]. Thus, the coexposed {101} and {001} facets on a single anatase TiO<sub>2</sub> nanocrystal can form a surface heterojunction,

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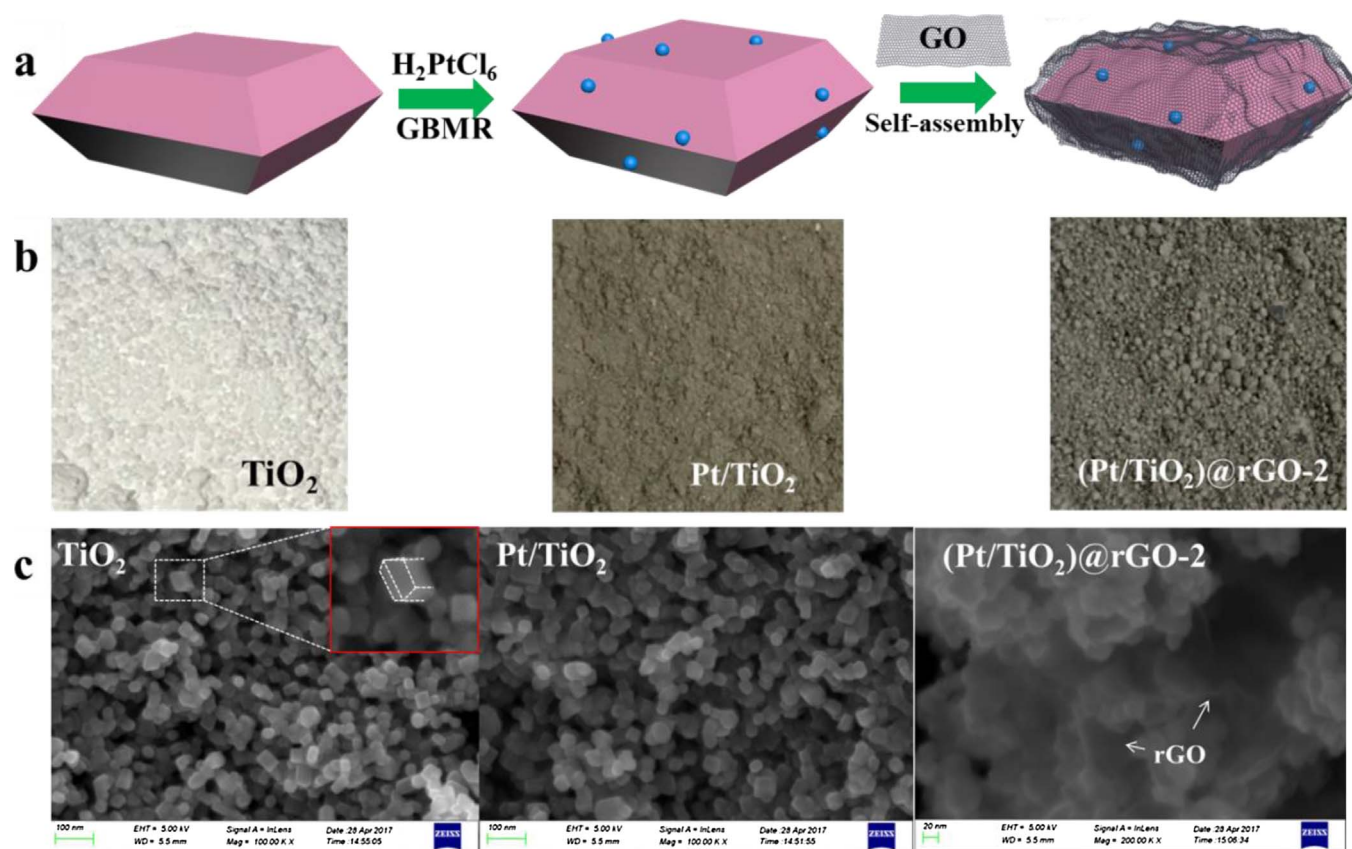


Fig. 1. The schematic for the two step synthesis of supported Pt NPs and wrapping rGO shells on the surface of TiO<sub>2</sub> nanocrystals (a). The digital photograph (b) and SEM images (c) of TiO<sub>2</sub>, Pt/TiO<sub>2</sub> and (Pt/TiO<sub>2</sub>)@rGO-2 catalysts.

which is favorable to the separation of photogenerated charges. Anatase TiO<sub>2</sub> nanocrystals with an optimal percentage of {101} and {001} facets can further improve separation of photogenerated carriers and enhance photocatalytic activity [20], and the ultrafine TiO<sub>2</sub> nanocrystals with small size and large surface area can further improve the photocatalytic activity for CO<sub>2</sub> reduction to methane (CH<sub>4</sub>) due to the increasing active sites on the surface of crystal facets heterojunction [21]. However, the photocatalytic activity of single TiO<sub>2</sub> nanocrystal for CO<sub>2</sub> reduction is not efficient enough to the industrialized application because of the low selectivity and production rate, which is related to the rapid recombination of photogenerated charges and the insufficient surface adsorption sites for CO<sub>2</sub> and H<sub>2</sub>O [22–24].

Based on the reaction nature of the photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O, the product of one CH<sub>4</sub> molecule requires eight electrons, eight hydrogen protons and one CO<sub>2</sub> molecule. Thus, the surface enrichments of photogenerated electrons and adsorbed reactant molecules are very critical for improving formation rate and selectivity of CH<sub>4</sub> product [25]. It is generally strategy that supported noble metal nanoparticles (NPs) could suppress the recombination of photogenerated charges and improve the utilization efficiency of photogenerated electrons [26–29]. Due to the Fermi levels of Pt NPs below the conduction band edge of TiO<sub>2</sub> energetically, photogenerated electrons in the conduction band (CB) of TiO<sub>2</sub> can be rapidly transferred and trapped on the surface of supported Pt NPs as a reservoir of photoelectrons [30,31]. Thus, supported Pt NPs as electron trap are beneficial to improve photogenerated charge separation and photocatalytic activity, especially to the formation of H<sub>2</sub> product from water splitting via bi-electron reduction process. However, the improving selectivity of CH<sub>4</sub> product is still a challenge due to its low capability of adsorption and activation for CO<sub>2</sub> reactant.

Recently, the graphene materials can play important roles in improving the photocatalytic performance, including co-catalyst [32,33],

photosensitizer [34,35], coupler [36,37] and photocatalysts [38–43]. It has been demonstrated that graphene as a high-efficiency acceptor and transporter of electron is potential to further improve the separation efficiency of photogenerated electrons and holes in artificial photosynthesis reaction [44–47]. Moreover, the graphene oxide materials with the surface hydroxyl and extended  $\pi$  bond can enhance the adsorption and activation capacity for CO<sub>2</sub> and H<sub>2</sub>O molecules. Integrating the above preminent properties, the construction of rGO-Pt-TiO<sub>2</sub> ternary nanojunction combined with optimal percent of coexposed {001}-51% and {101}-49% facets for photogenerated charges separation. The all-solid-state electron multiple transmission system with TiO<sub>2</sub>(core)-Pt(mediator)-rGO(shell) nanojunction can achieve the high-efficiency separation of photogenerated electrons and holes via the two-step vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO, which exhibits ternary system far exceeding the unitary or binary systems. It suggests that (Pt/TiO<sub>2</sub>)@rGO catalysts are an excellent system not only for surface chemical processes occurred at the interfaces of reactant and catalyst, but also for light-chemical energy conversion.

Herein, the core-shell-structured photocatalysts of Pt/TiO<sub>2</sub> nanocrystals wrapped by reduced graphene oxide (rGO) ultrathin sheets ((Pt/TiO<sub>2</sub>)@rGO) were synthesized by a self-assembly method of a simple and pure chemical bonding reactions. The core part of well-defined core-shell structure is the truncated octahedral bipyramid anatase TiO<sub>2</sub> nanocrystal with optimized proportion of coexposed {001}-51% and {101}-49% facets for photogenerated charges separation. The all-solid-state electron multiple transmission system with TiO<sub>2</sub>(core)-Pt(mediator)-rGO(shell) nanojunction can achieve the high-efficiency separation of photogenerated electrons and holes via the two-step vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO, which exhibits ternary system far exceeding the unitary or binary systems. It suggests that (Pt/TiO<sub>2</sub>)@rGO catalysts are an excellent system not only for surface chemical processes occurred at the interfaces of reactant and catalyst, but also for light-chemical energy conversion.

## 2. Experimental section

### 2.1. Sample preparation

The core-shell-structured (Pt/TiO<sub>2</sub>)@rGO photocatalysts were

designed and practical fabricated by a self-assembly method of a simple and pure chemical bonding reactions (detailed in the *Supplementary Information of Sample Preparation*), and the schematic representation and digital photographs of the preparation processing for (Pt/TiO<sub>2</sub>)@rGO core-shell photocatalysts are shown in Fig. 1. As shown in Fig. 1a, the typical procedures with three steps were described as follows: Firstly, the truncated octahedral bipyramid anatase TiO<sub>2</sub> nanocrystal with coexposed {001}-51% and {101}-49% facets were synthesized by two steps of hydrothermal processes using commercial P25 as Ti source reported by Cao et al. [21]. As shown in Fig. 1b of digital photographs, anatase TiO<sub>2</sub> nanocrystal with white color was obtained after washed, dried and calcined processes. Secondly, Pt NPs supported on anatase TiO<sub>2</sub> nanocrystals were prepared by the gas bubbling-assisted membrane reduction (GBMR) method using the poly (N-vinyl-2-pyrrolidone) (PVP) as the protecting agent and the NaBH<sub>4</sub> solution as the reducing agent (Fig. S1). The GBMR process can control the nucleation and growth processes of Pt nucleus on the surface of anatase TiO<sub>2</sub> nanocrystals via highly homogeneous dispersion of reductant using the ceramic membrane tubes. And it is also critical process that [PtCl<sub>6</sub>]<sup>2-</sup> ions are adsorbed and anchored on surface [OH<sub>2</sub>]<sup>+</sup> groups of anatase TiO<sub>2</sub> nanocrystals, because the pH value of mixture solution (~3.0) using the adjustment of HCl solution is lower than the isoelectric point (IEP) of TiO<sub>2</sub>. After supported Pt NPs, the color of samples changed from white to light gray in Fig. 1b. The loading amounts of supported Pt NPs in the photocatalyst is 1.0 wt% in theory. Thirdly, the core-shell-structured photocatalysts of Pt/TiO<sub>2</sub> nanocrystals wrapped by rGO sheets were synthesized by a self-assembly method of a simple and pure chemical bonding reactions. Graphite oxide (GO) was prepared by the traditional Hummers method from graphite power (Fig. S2), and the exfoliated GO shows super electronic conductivity because of the  $\pi$ -system interruption by substitution with a numerous defects (oxygen functional groups) [48], thus, GO dispersed in ethyl alcohol are strongly adsorbed on the surface of Pt/TiO<sub>2</sub> nanocrystals due to surface condensation reaction of oxygen-containing functional groups. Then, GO/(Pt/TiO<sub>2</sub>) samples were reduced to rGO using NaBH<sub>4</sub> solutions [49]. Finally, the desired core-shell structured (Pt/TiO<sub>2</sub>)@rGO catalysts with dark gray (Fig. 1b) were obtained after centrifugation, wash and dry in a vacuum oven at 60 °C for 12 h. The catalysts are uniformly named as (Pt/TiO<sub>2</sub>)@rGO-n, where n is the nominal weight percent of rGO to Pt/TiO<sub>2</sub> (1, 2, 5 and 10 wt% of Pt/TiO<sub>2</sub>).

## 2.2. Characterization

The morphology and microscopic structure information were obtained on a scanning electron microscope (SEM, FEI Quanta 200F) and a transmission electron microscope (TEM, JEOL JEM 2100) equipped with a field emission source at an accelerating voltage of 200 kV. The nitrogen adsorption/desorption isotherm was carried out at -196 °C by using an automated gas sorption analyzer (Quantachrome Autosorb-iQ, USA) after having degassed the sample for 4 h at 300 °C. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method. The crystal phase properties of all as-prepared samples were analyzed with a powder X-ray diffractometer (Shi-madzu XRD 6000) and a Renishaw Micro-Raman System 2000 spectrometer. The laser line of Raman microscope was 532 nm. X-ray photoelectron spectra (XPS) were acquired by a Perkin-Elmer PHI-1600 ESCA spectrometer with Mg K $\alpha$  emission. Photoluminescence (PL) spectra were recorded using the Edinburgh Instruments Xe900 equipped with a Xe lamp and the excitation wavelength was set at 380 nm. Photoelectrochemical (PEC) measurements were performed on an electrochemical workstation (CHI660E) in the saturated solution of Na<sub>2</sub>SO<sub>4</sub>, which has a three-electrode configuration and all as-prepared samples, the saturated Ag/AgCl, a platinum foil were employed to as working photoelectrode, reference and counter electrode, respectively. The samples were illuminated under a 300 W Xe lamp. Temperature-programmed desorption of carbon dioxide (CO<sub>2</sub>-TPD) measurement was performed on a

conventional flow apparatus. Prior to measurements, 100 mg of the sample was pretreated in Ar gas (60 cm<sup>3</sup> min<sup>-1</sup>) at 150 °C for 1 h and then cooled down to room temperature. Next, the sample was exposed to CO<sub>2</sub> flow of 30 cm<sup>3</sup> min<sup>-1</sup> for 0.5 h to ensure the sufficient adsorption of CO<sub>2</sub>. Before desorption, the sample was flushed in Ar gas for 1 h. Subsequently, CO<sub>2</sub> desorption was performed in the range of 30–400 °C at a heating rate of 10 °C min<sup>-1</sup> under an Ar flow of 30 cm<sup>3</sup> min<sup>-1</sup>. In-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) were recorded using a thermo Nicolet IS50 spectrometer, which was equipped with a high temperature environmental cell fitted with Zn-Se window and an MCT detector cooled with liquid N<sub>2</sub>. The catalyst was loaded in the Harrick IR cell and heated to 200 °C under N<sub>2</sub> at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup> for 60 min to remove adsorbed impurities. Then the catalyst was cooled down to 30 °C. A background spectrum was collected under a flowing N<sub>2</sub> atmosphere and was subtracted from the sample spectra. Next, the sample was exposed to CO<sub>2</sub> flow of 50 cm<sup>3</sup> min<sup>-1</sup> for 30 min and then under N<sub>2</sub> at a flow rate of 50 cm<sup>3</sup> min<sup>-1</sup> for 30 min. The in-situ DRIFTS spectra were recorded by accumulating 64 scans with a resolution of 4 cm<sup>-1</sup>. Density functional theory (DFT) calculation was carried out by the Vienna ab initio simulation package (VASP) in order to elucidate relationship between the origin of visible absorption and oxygen defects. The calculations involved on-site Coulomb corrections (DFT + U, U = 4.2 eV for Ti 3d states). [50] PAW pseudopotential was used to describe the core-valence electron interaction. Plane-wave basis set with an energy cutoff of 400 eV was used in this work. Anatase TiO<sub>2</sub> (001) facet was presented by a five-layer slab model with a vacuum gap of 15 Å. For all the surface calculations, the model was a periodic slab with a (2 × 2) surface unit cell. A Monkhorst pack 6 × 6 × 1 k-point mesh was used for the Brillouin zone integration. During structural optimizations, all of the atoms except those in the bottom TiO<sub>2</sub> two layers of the slab were allowed to relax until atom forces were smaller than 0.05 eV Å<sup>-1</sup>.

## 2.3. Photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O test

Photocatalytic CO<sub>2</sub> reduction test was carried out in a gas-closed circulation system (Perfect Light Company, Beijing, China) irradiated under a 300 W Xe lamp (320–780 nm). The certain amount of catalysts was uniformly dispersed on a watch-glass with 6.5 cm basal diameter. Before the light irradiation, the photo reactor system was thoroughly vacuum-treated, then CO<sub>2</sub> gas was introduced into the circulation system. The deionized water (2 mL) was injected into the bottom of the reactor. The intensity of incident light was measured to be 80 mW cm<sup>-2</sup> by a spectroradiometer. During the light irradiation in 8 h, the amounts of H<sub>2</sub>, CO, and hydrocarbons in the reactor were analyzed by an online gas chromatograph (GC-9560; HuaAiSePu Corp., Shanghai, China) with a flame ionization detector (FID) and a thermal conductivity detector (TCD) each 60 min intervals. The gas products were analyzed by the external standard method. The apparent quantum efficiency (AQE) was measured under the similar photocatalytic reaction condition, and the irradiation light (wavelength 380 nm) using a band-pass filter (full width at half maximum 15 nm) was used as the light source. The incident flux was determined by Radiometer (FZ-A, Photoelectric Instrument Factory of Beijing Normal University). The AQE values for CH<sub>4</sub> evolution of CO<sub>2</sub> reduction were calculated according to the following equation:

$$\Phi_{\text{CH}_4} (\%) = \frac{8 \times [\text{the number of evolved CH}_4 \text{ molecules}]}{[\text{number of incident photons}]} \times 100\%$$

## 3. Results

### 3.1. The characterization results of the catalysts

Fig. 1 shows the schematic, digital photographs and SEM images for synthesis procedures of (Pt/TiO<sub>2</sub>)@rGO-n catalysts. With progressing of



the preparation process, the color of prepared samples has changed obviously from white to light gray and even dark gray in Fig. 1b. It indicates that the surface of anatase  $\text{TiO}_2$  nanocrystals with white color are deposited successively by Pt NPs and rGO sheets with black color. As shown in Fig. 1c of SEM images, pure anatase  $\text{TiO}_2$  nanocrystals show the homogeneously truncated octahedral bipyramid structure with bare surface clearly. The average particle size of  $\text{TiO}_2$  nanocrystals is 30 nm estimated by counting more than 100 nanoparticles. And the truncated octahedral bipyramid nanostructure of  $\text{TiO}_2$  nanocrystal is not influenced by supported Pt nanoparticles via the synthesis process of GBMR method. After further introduction of rGO sheets, the truncated octahedral bipyramid morphology is obscured, and the Pt/ $\text{TiO}_2$ -wrapped ultrathin rGO nanolayer catalysts present a wrinkle-like morphology uniformly, indicating that the core-shell structure of Pt/ $\text{TiO}_2$  nanocrystals wrapped by rGO sheets can be obtained by a pure chemical bonding reaction successfully. With increasing of the mass ratios of rGO/ $\text{TiO}_2$ , the surface feature of truncated octahedral bipyramid nanocrystals become indistinct and even disappear due to the excess wrapped by rGO sheets (Fig. S3).

The phase structures of  $\text{TiO}_2$ , Pt/ $\text{TiO}_2$ ,  $\text{TiO}_2$ @rGO-2 and (Pt/ $\text{TiO}_2$ )@rGO-n catalysts were investigated by XRD patterns and the results are shown in Fig. 2. The diffraction peaks (2 $\theta$ ) of  $\text{TiO}_2$  nanocrystals at 25.3, 37.8, 48.0, 53.9, 55.1, 62.7 and 75.0° can be indexed to the (101), (004), (200), (105), (211), (204) and (215) crystal facets of anatase-phase  $\text{TiO}_2$  (PDF# 21-1272), respectively. There is not any diffraction peak corresponding to other phase of  $\text{TiO}_2$ , indicating that the phase structure of anatase  $\text{TiO}_2$  nanocrystal is single and pure. After introduction of supported Pt NPs, the diffraction peaks belonging to  $\text{TiO}_2$  did not change, and the characteristic diffraction peaks of Pt NPs were not detected. The above-mentioned results indicate that the sizes or loadings of supported Pt NPs are smaller than the detection limit of XRD spectra for supported nanoparticles. Meanwhile, no diffraction peaks for carbon species were observed in  $\text{TiO}_2$ @rGO and (Pt/ $\text{TiO}_2$ )@rGO samples, which might be due to the relatively low diffraction intensity of graphene. No obvious change of its crystalline phase is observed after Pt NPs deposited and rGO sheets coated on  $\text{TiO}_2$  nanoparticles. In addition, Table S1 shows the structural physical parameters of  $\text{TiO}_2$ , Pt/ $\text{TiO}_2$ ,  $\text{TiO}_2$ @rGO-2 and (Pt/ $\text{TiO}_2$ )@rGO-n catalysts including surface areas, pore volumes, crystal parameters and Pt actual contents. After introduction of supported Pt NPs and wrapping rGO sheets, the surface areas and pore volumes of the catalysts have not changed obviously, and the Pt actual contents in the catalysts determined by ICP-AES are always in the range of 0.8–0.9 wt%.

Raman spectroscopy is an excellent characterization technique to further observe the phase structure of  $\text{TiO}_2$  and rGO sheets owing to its strong scattering properties. As shown in Fig. 3, Raman spectra of all the samples show several characterized bands located at 144, 397, 517, and 638  $\text{cm}^{-1}$ , which is assigned to the  $E_{g(1)}$ ,  $B_{1g(1)}$ ,  $A_{1g}$  +  $B_{1g(2)}$ , and

$E_{g(2)}$  modes of anatase phase of  $\text{TiO}_2$ , respectively [51]. The single anatase phase structure of  $\text{TiO}_2$  support is further confirmed. After introduction of wrapping rGO nanolayers, it is worth noting that two typical bands centered at 1347 and 1590  $\text{cm}^{-1}$  are observed obviously, which is assigned to the D-band and G-band of the graphitized structure of rGO sheets, respectively. With the increasing of wrapping rGO contents, the intensity of the characteristic bands of anatase  $\text{TiO}_2$  nanocrystals decreases gradually and even disappears for the (Pt/ $\text{TiO}_2$ )@rGO-10 catalyst, which is direct evidence of Pt/ $\text{TiO}_2$  nanocrystals wrapped by rGO sheets and the formation of (Pt/ $\text{TiO}_2$ )@rGO core-shell structure. On the other hand, with the increasing of rGO content, the thickness of rGO in the core-shell structure grows larger gradually.

In order to further investigate the physical structure, TEM and HRTEM images of  $\text{TiO}_2$ , Pt/ $\text{TiO}_2$  and (Pt/ $\text{TiO}_2$ )@rGO-n catalysts are shown in Fig. 4. For  $\text{TiO}_2$  nanocrystals, the hexagons as projection of truncated octahedral bipyramid are exhibited. The lateral isosceles trapezoid of the truncated octahedral bipyramid nanocrystals corresponds to {101} facet, and the top and bottom facets are the {001} facet [52]. The interfacial angle between {101} and {001} facets is 68.3°. The mean particle size of anatase  $\text{TiO}_2$  nanocrystal is about 30 nm in accordance with SEM results. As shown in inset of Fig. 4a, the lattice spacings paralleled to the lateral and the top faces are ca. 0.35 and 0.24 nm, which are corresponding to the {101} and {004} facets of anatase  $\text{TiO}_2$ , respectively. Anatase  $\text{TiO}_2$  nanocrystal was estimated to be coexposed {001}-51% and {101}-49% facets as calculated by a reported method [53]. The coexposed {101} and {001} facets on a single anatase  $\text{TiO}_2$  nanocrystal can form a surface heterojunction owing to different surface energy and band edge positions, which are favorable for the separation of photogenerated carriers. For Pt/ $\text{TiO}_2$  catalysts, a mass of bare Pt NPs supported on the surface of  $\text{TiO}_2$  nanocrystals can be clearly observed in Fig. 4b, and the average diameter of Pt NPs with a narrow distribution is 3.3 nm. As shown in inset of Fig. 4b, the lattice fringes (0.22 nm) of one hemispherical Pt NP exhibit clearly the exposed (111) facet, and the crystal fusion domain at the phase interface of Pt- $\text{TiO}_2$  shows a strong lattice distortion. It indicates that there is a tight contact interface between Pt NPs and  $\text{TiO}_2$  nanocrystals, which is beneficial to the subsequent efficient electron transfer and rGO shell coating.

After introduction of rGO sheets, it is observed clearly that the Pt/ $\text{TiO}_2$  nanocrystals are wrapped by rGO sheets and the core-shell structure of (Pt/ $\text{TiO}_2$ )@rGO catalysts is fabricated. For (Pt/ $\text{TiO}_2$ )@rGO-1 catalyst in Fig. 4c, Pt/ $\text{TiO}_2$  nanocrystals are not wrapped completely owing to insufficient amount of wrapping rGO sheets. With increasing of rGO sheets, the uniform core-shell structure of (Pt/ $\text{TiO}_2$ )@rGO catalysts is found. In Fig. 4d, it exhibited clearly the core-shell structure of Pt/ $\text{TiO}_2$  nanocrystals wrapped by graphitic layers of rGO, and supported Pt NPs as intermedium are sandwiched between rGO shell and  $\text{TiO}_2$  core. The thickness of rGO shell is in the range of 0.4–1.1 nm, which is equal to the thickness of 1–3 layers of single-layer rGO (0.34 nm) in inset of Fig. 4d. It is in accord with TEM images of  $\text{TiO}_2$ @rGO-2 catalyst in Fig. S5. After further increasing of wrapping rGO sheets, the thickness of rGO shell increases gradually, i.e., the average thicknesses of rGO shell over (Pt/ $\text{TiO}_2$ )@rGO-5 and (Pt/ $\text{TiO}_2$ )@rGO-10 catalysts are 2.5 and 5.0 nm, respectively.

The morphology and composition of (Pt/ $\text{TiO}_2$ )@rGO-2 catalyst were further characterized by the HAADF-STEM and EDS elemental mapping, and the result is shown in Fig. 4g. The four elements of Pt, O, Ti and C in the (Pt/ $\text{TiO}_2$ )@rGO-2 catalyst were detected by SEM-EDS spectroscopy (Fig. S6). Supported Pt NPs are homogeneously dispersed on the surface of  $\text{TiO}_2$  supports, which is in agreement with the result of TEM images. The compositional distributions of each element in the select local area of (Pt/ $\text{TiO}_2$ )@rGO-2 NPs reveal further obviously the tri-component core-shell-structured NPs with the core rich in Pt (sapphire) and the shell rich in carbon (dark red), and Ti and O elements in the local area of Pt NPs are rare in comparison with surrounding. It indicates that Pt NP is deposited on the surface of  $\text{TiO}_2$  and

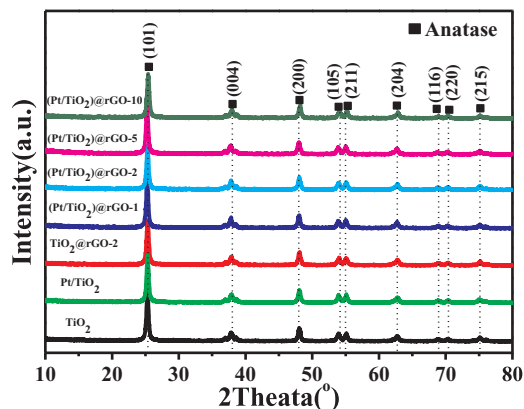


Fig. 2. XRD patterns of  $\text{TiO}_2$ , Pt/ $\text{TiO}_2$ ,  $\text{TiO}_2$ @rGO-2 and (Pt/ $\text{TiO}_2$ )@rGO-n catalysts.

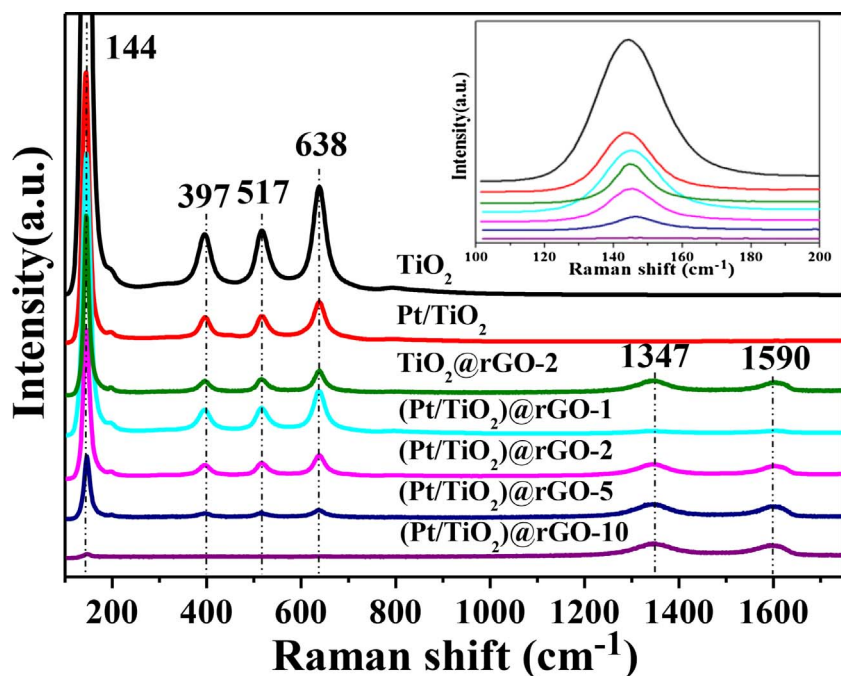


Fig. 3. Raman spectra of  $\text{TiO}_2$ ,  $\text{Pt/TiO}_2$ ,  $\text{TiO}_2@\text{rGO-2}$  and  $(\text{Pt/TiO}_2)@\text{rGO-n}$  catalysts.

subsequently is wrapped by rGO sheets. In other words, it is realized the formation of the core-shell structured  $(\text{Pt/TiO}_2)@\text{rGO}$  catalysts. Therefore, a  $\text{rGO}(\text{shell})\text{-Pt}(\text{core})\text{-TiO}_2(\text{core})$  nanojunction system with a tight electronic contact ensures the efficient photogenerated electron transfer and the subsequent photocatalysis.

To examine the effect of core-shell structured  $(\text{Pt/TiO}_2)\text{-rGO}$  nanojunction on the electronic properties of the surface elemental (Ti, O, Pt and C), XPS spectroscopy was carried out and the results are shown in Fig. 5. As shown in Fig. 5a, the binding energies of  $\text{Ti } 2p_{3/2}$  and  $\text{Ti } 2p_{1/2}$  in  $\text{TiO}_2$  nanocrystals are located at 457.8 and 463.5 eV, which is mainly assigned to  $\text{Ti}^{4+}$  species [54]. With increasing of rGO shell thickness in  $(\text{Pt/TiO}_2)@\text{rGO-n}$  catalysts, the intensities of  $\text{Ti } 2p$  XPS peaks decrease slightly, and the peaks have a positive shift gradually, which is attributed to the strong interactions of  $\text{TiO}_2\text{-Pt-rGO}$  ternary system. For  $\text{O } 1s$  XPS spectra in Fig. 5b, the curves exhibit one dominating peak at 528.8 eV and one secondary peak at 530.6 eV, which is ascribed to  $\text{Ti-O}$  bonding and surface  $\text{O-H}$  bonding of  $\text{TiO}_2$ , respectively [55]. The deconvolution of  $\text{O } 1s$  XPS spectrum of the  $(\text{Pt/TiO}_2)@\text{rGO-2}$  catalyst obtained by the standard procedure is shown in Fig. S7. Four peaks of binding energies located at 529.1, 529.7, 530.8, and 531.8 eV have been fitted, which are ascribed to  $\text{Ti-O-Ti}$  (lattice O),  $\text{C-O-Ti}$ ,  $\text{Ti-OH}$ , and  $\text{C-OH}$  (and  $\text{C-O-C}$ ) species, respectively [56]. Being same as the  $\text{Ti } 2p$  spectra, the  $\text{Ti-O-Ti}$  peaks for  $(\text{Pt/TiO}_2)@\text{rGO}$  catalysts also have a positive shift in comparison with  $\text{TiO}_2$  nanocrystals, which further proves the strong interactions and the electron transfer in the ternary system.

Fig. 5c shows  $\text{Pt } 4f$  XPS spectra of  $\text{Pt/TiO}_2$  and  $(\text{Pt/TiO}_2)@\text{rGO-n}$  catalysts. In order to observe clearly, the peak intensities of  $(\text{Pt/TiO}_2)@\text{rGO-2}$  and  $(\text{Pt/TiO}_2)@\text{rGO-10}$  catalysts are magnified to 1.5 and 2.0 times, respectively. After introduction of wrapping rGO sheets, the intensities of  $\text{Pt } 4f$  XPS peaks decrease obviously due to the shielding effect of rGO shell, which is also indirect evidence to the formation of  $(\text{Pt/TiO}_2)@\text{rGO}$  core-shell structure. The deconvolutions of the spectra were made by the standard procedure, and the binding energies of 70.2 and 73.5 eV, 71.2 and 74.8 eV, 74.1 and 76.9 eV correspond to  $\text{Pt}^0$ ,  $\text{Pt}^{2+}$  and  $\text{Pt}^{4+}$  species, respectively. It indicates that the metallic ( $\text{Pt}^0$ ) and ionic ( $\text{Pt}^{2+}$ ) species coexist in  $(\text{Pt/TiO}_2)@\text{rGO-n}$  catalysts. The formation of ionic  $\text{Pt}^{2+}$  ( $\text{Pt}^{2+}$  and  $\text{Pt}^{4+}$ ) species are derived from the electron transfer from  $\text{Pt}^0$  to  $\text{O}^{2-}$  due to the strong interaction between metal (Pt)-support (rGO and  $\text{TiO}_2$ ), which is beneficial to the vectorial

electron transfer from excitation of  $\text{TiO}_2$  to rGO driven by the two steps using Pt NPs as conducting medium [57]. The relative proportions of  $\text{Pt}^0$ ,  $\text{Pt}^{2+}$  and  $\text{Pt}^{4+}$  species on the surface of catalysts were estimated and presented in Table. 1. The surface  $\text{Pt}^{2+}$  concentration of  $(\text{Pt/TiO}_2)@\text{rGO-2}$  (47.1%) and  $(\text{Pt/TiO}_2)@\text{rGO-10}$  (51.5%) catalysts are significantly higher than that of  $\text{Pt/TiO}_2$  catalyst (29.9%), which is attributed to the strong electron transfer of  $(\text{Pt/TiO}_2)@\text{rGO-n}$  core-shell catalyst from Pt NPs to rGO shell. Corresponding to the  $\text{C } 1s$  XPS spectra in Fig. 5d, the  $\text{C } 1s$  peak is dominated by elemental carbon at 283.9 eV, assigned mainly to the  $\text{C-C}$ ,  $\text{C=C}$  and  $\text{C-H}$  bonds ( $\text{sp}^2$ ) of graphene [58]. The other two peaks at 285.7 and 287.8 eV are assigned to the  $\text{C-O}$  and  $\text{O-C=O}$  species, respectively [59]. And the  $\text{C } 1s$  peak at  $\sim 281$  eV corresponding to  $\text{Ti-C}$  bond is not observed, indicating that carbon atom did not directly enter into bulk  $\text{TiO}_2$  lattice [60]. All of the element peaks are shifted to higher binding energy values than that for the pure  $\text{TiO}_2$ , providing evidence of a strong interaction among  $\text{rGO-Pt-TiO}_2$  ternary components, which is conducive to propelling the photogenerated electrons transfer from  $\text{TiO}_2$  to rGO using Pt NPs as a medium.

In order to further observe the functional groups and chemical bonds of  $\text{Ti-O-Ti}$  vibrations and  $\text{Ti-O-C}$  vibrations, the Fourier transform infrared (FTIR) spectra of GO,  $\text{TiO}_2$  and  $(\text{Pt/TiO}_2)@\text{rGO-n}$  catalysts were investigated and the result is shown in Fig. 6. For comparison, the FTIR spectrum of GO is included. In the case of GO, there are five characteristic absorption bands in the region of  $1000\text{--}3500\text{ cm}^{-1}$ . The absorption bands at 1048, 1392, 1628, 1726, and  $3432\text{ cm}^{-1}$  were attributed to the  $\text{C-O}$  alkoxy,  $\text{O=C-O}$  carboxyl,  $\text{C=C}$  (skeleton of GO),  $\text{C=O}$  carbonyl and  $\text{O-H}$  stretching, respectively [61]. For pure  $\text{TiO}_2$ , the spectrum shows a broad absorption peak around  $500\text{ cm}^{-1}$ , which was attributed to the  $\text{Ti-O-Ti}$  stretching vibrations. The presence of absorption bands around  $3400$  and  $1627\text{ cm}^{-1}$  were attributed to the  $\text{O-H}$  stretching frequency, which came from the surface hydroxyl groups and the adsorbed water molecules. For  $(\text{Pt/TiO}_2)@\text{rGO-2}$  and  $(\text{Pt/TiO}_2)@\text{rGO-10}$  catalysts, the intensity of absorption band at  $1726\text{ cm}^{-1}$  corresponding to the oxygen functional groups decreased dramatically and even disappeared. The presence of absorption bands below  $1000\text{ cm}^{-1}$  was attributed to the  $\text{Ti-O-Ti}$  and  $\text{Ti-O-C}$  stretching vibrations [62]. As a result, the chemically bond of  $\text{Ti-O-C}$  were formed by the residual carboxylic groups ( $\text{COOH}$ ) on GO sheets interacted with the surface hydroxyl groups



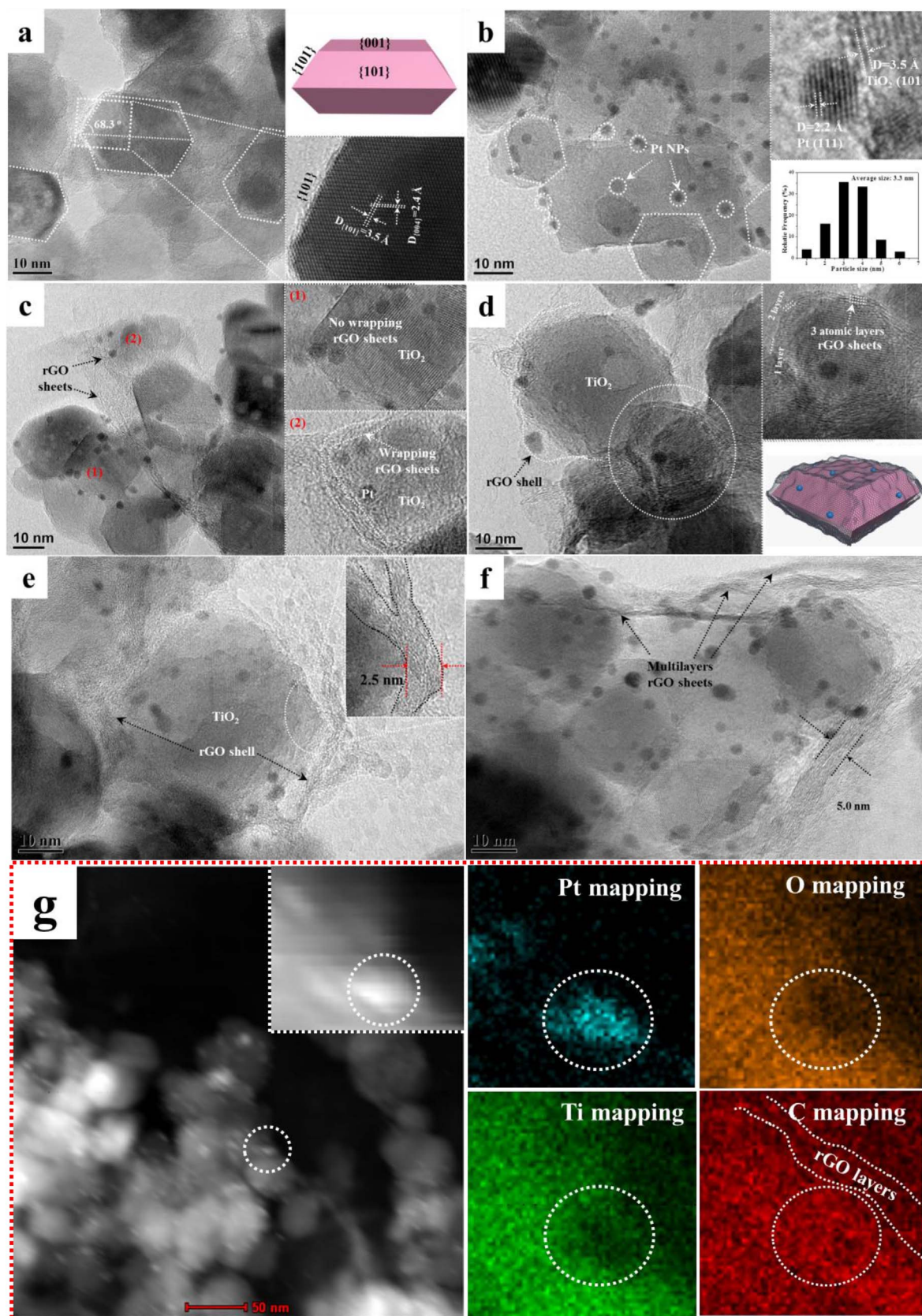


Fig. 4. TEM and HRTEM images of  $\text{TiO}_2$  (a),  $\text{Pt}/\text{TiO}_2$  (b),  $(\text{Pt}/\text{TiO}_2)@\text{rGO}-1$  (c),  $(\text{Pt}/\text{TiO}_2)@\text{rGO}-2$  (d),  $(\text{Pt}/\text{TiO}_2)@\text{rGO}-5$  (e) and  $(\text{Pt}/\text{TiO}_2)@\text{rGO}-10$  (f) catalysts. HAADF-STEM and EDS elemental mapping images of  $(\text{Pt}/\text{TiO}_2)@\text{rGO}-2$  catalyst (g).

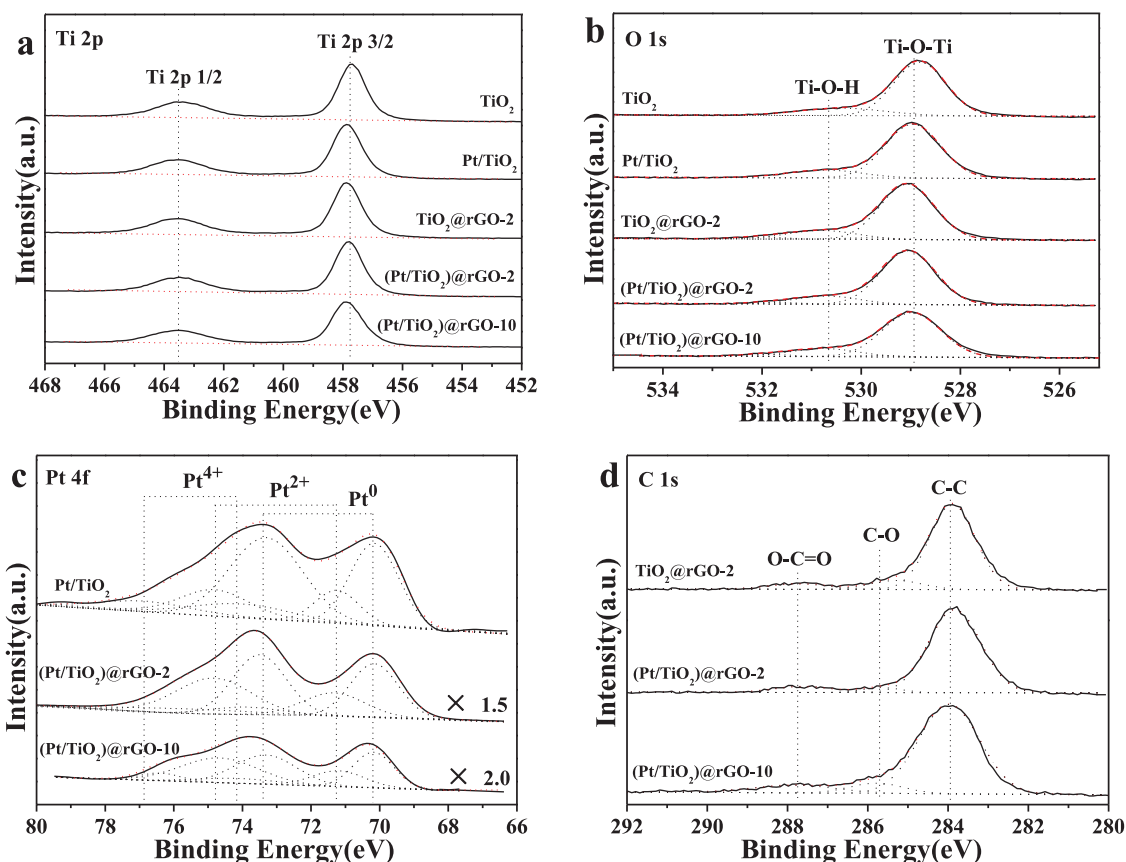


Fig. 5. XPS of Ti 2p (a), O 1s (b), Pt 4f (c) and C 1s (d) spectra of GO, TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, TiO<sub>2</sub>@rGO-2 and (Pt/TiO<sub>2</sub>)@rGO-n catalysts. For clear comparison, the XPS Pt 4f intensities of (Pt/TiO<sub>2</sub>)@rGO-2 and (Pt/TiO<sub>2</sub>)@rGO-10 in (c) are magnified to 1.5 and 2.0 times, respectively.

**Table 1**  
Surface compositions and oxidation states of Pt species derived from XPS analyses.

Samples	Pt species (%)			
	Pt <sup>0</sup>	Pt <sup>2+</sup>	Pt <sup>4+</sup>	Pt <sup>k+</sup> <sup>a</sup>
Pt/TiO <sub>2</sub>	70.1	20.3	9.6	29.9
(Pt/TiO <sub>2</sub> )@rGO-2	52.9	36.7	10.4	47.1
(Pt/TiO <sub>2</sub> )@rGO-10	48.5	40.1	11.4	51.5

<sup>a</sup> The Pt<sup>k+</sup> values are equal to the sum of Pt<sup>2+</sup> and Pt<sup>4+</sup>.

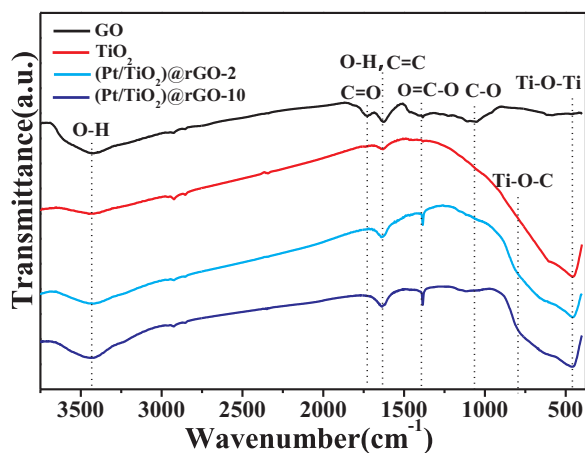


Fig. 6. FTIR spectra of GO, TiO<sub>2</sub> and (Pt/TiO<sub>2</sub>)@rGO-n catalysts.

(Ti—OH) of TiO<sub>2</sub> during mixing GO with TiO<sub>2</sub> nanocrystals. In addition, the intensity of Ti—O—Ti bands absorption band weakened obviously with the increasing of rGO content, which further confirmed that the rGO sheets wrapped on the surface of TiO<sub>2</sub> nanoparticles in accordance with the Raman, TEM and XRD results.

The optical absorption properties of TiO<sub>2</sub>, Pt/TiO<sub>2</sub> and (Pt/TiO<sub>2</sub>)@rGO-n catalysts were investigated by means of UV–vis DRS and the result is shown in Fig. 7. For comparison, the commercial P25 is also included. Compared with limited visible light adsorption and wide band gap (~3.1 eV) of commercial P25, anatase TiO<sub>2</sub> nanocrystals show the strong absorption intensity in visible range, which is attributed to the existence of surface oxygen defects due to the presence of enlarged Ti—O—Ti bond angles and a mass of active unsaturated coordination Ti atoms on the {001} facet of anatase TiO<sub>2</sub> nanocrystals [63]. In order to elucidate relationship between the origin of visible absorption and oxygen defects, Fig. S8 shows the surface density of states (DOS) for TiO<sub>2</sub>(001) and TiO<sub>2</sub>(001) with an oxygen vacancy obtained by DFT calculation using VASP. TiO<sub>2</sub> with an oxygen vacancy (TiO<sub>2-x</sub>) has one more peak near Fermi level compared with the stoichiometric TiO<sub>2</sub>, indicating that the surface of TiO<sub>2-x</sub> is higher valence band energy level. Therefore, TiO<sub>2-x</sub> needs lower energy to excite photogenerated electrons from valence band to conduction band. In other words, the photons in visible region can be absorbed by TiO<sub>2</sub> with an oxygen vacancy, but the stoichiometric TiO<sub>2</sub> cannot. Pt/TiO<sub>2</sub> catalyst possesses stronger visible light absorption and displays a slight red shift of absorption edge compared with anatase TiO<sub>2</sub> nanocrystals, which is ascribed to the localized surface plasmon resonance effect of supported Pt NPs on enhanced light-trapping efficiency [64]. After further introduction of wrapping rGO sheets, the visible light absorption intensities of (Pt/TiO<sub>2</sub>)@rGO-n catalysts are improved, indicating that wrapping rGO sheets can enhance the visible light absorption efficiency. The band

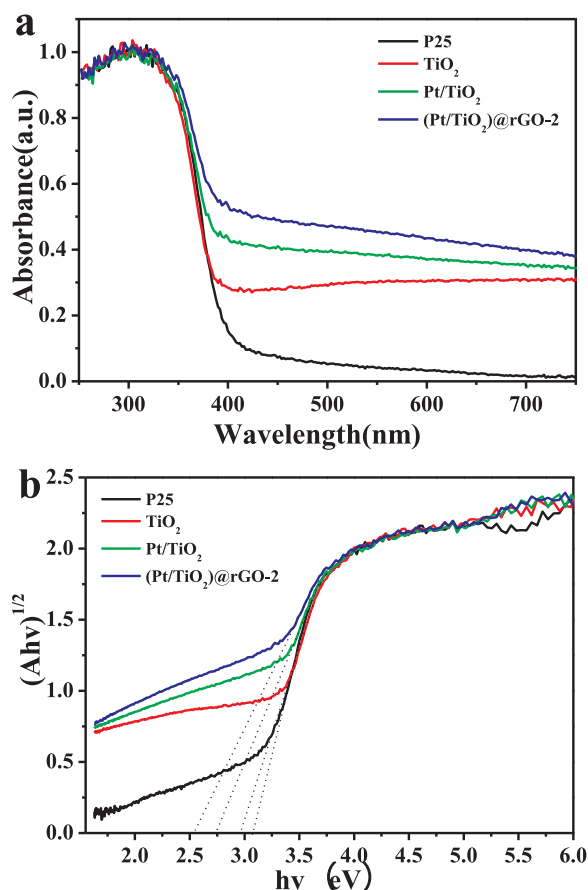


Fig. 7. UV-vis DRS (a) and Kubelka-Munk transformed reflectance spectra (b) of P25, TiO<sub>2</sub>, Pt/TiO<sub>2</sub> and (Pt/TiO<sub>2</sub>)@rGO-2 catalysts.

energy gap of samples could be calculated by the equation of  $(\alpha h\nu)^n = A(h\nu - E_g)$ , where  $\alpha$  is the absorption coefficient,  $h\nu$  is the absorption energy,  $A$  is the parameter that related to the effective masses associated with the valence and conduction bands,  $n$  is  $1/2$  for a direct transition and  $E_g$  is the band gap energy [65]. Fig. 7b shows the plotting  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  based on the spectral response in Fig. 7a, and the extrapolated intercept corresponds to  $E_g$  values. It is noted that the  $E_g$  value (2.95 eV) of anatase TiO<sub>2</sub> nanocrystals is smaller than commercial P25 (3.10 eV). And the  $E_g$  value of Pt/TiO<sub>2</sub> catalyst is only 2.75 eV due to an additional absorption band of supported Pt NPs in the visible region. After introduction of Pt NPs and rGO sheets, (Pt/TiO<sub>2</sub>)@rGO-2 catalyst shows the smallest optical band gap energy (2.55 eV), which is attributed to an additional absorption band of supported Pt NPs and rGO sheet in the visible region. Therefore, (Pt/TiO<sub>2</sub>)@rGO-n catalysts with enhanced visible-light absorption are promising for photocatalytic reaction.

PL spectroscopy is a common method to understand the fate of photogenerated electron-hole pairs in semiconductor catalysts and it is quite helpful to explore the efficiency of the charge carrier separation, migration, trapping and recombination. The intensity of PL emission spectrum represents the recombination of photogenerated electrons and holes, and the lower intensity exhibits the less recombination of electrons and holes. Fig. 8 exhibits the PL spectra of P25, TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, TiO<sub>2</sub>@rGO-2 and (Pt/TiO<sub>2</sub>)@rGO-n catalysts with the excitation wavelength of 380 nm. The emission peak centered at 390–550 nm is assigned to the emission of photogenerated electron-hole recombination. The PL emission intensity of anatase TiO<sub>2</sub> nanocrystals is lower than that of P25, indicating that the surface heterojunction between {001} and {101} facets in the single anatase TiO<sub>2</sub> nanocrystal can enhance transfer and separation of photogenerated electrons and holes. After

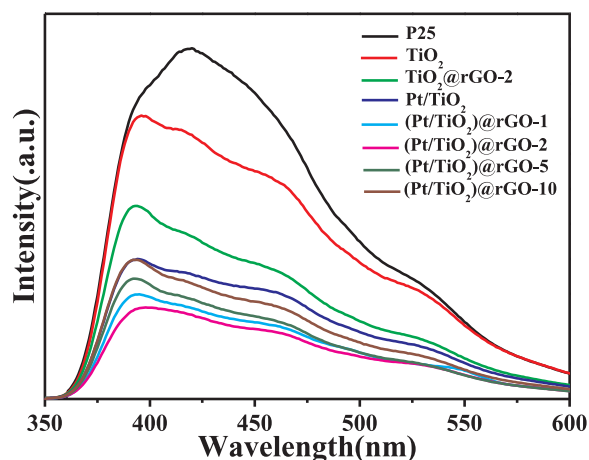


Fig. 8. Photoluminescence spectra ( $\lambda_{\text{ex}} = 380$  nm) of P25, TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, TiO<sub>2</sub>@rGO-2 and (Pt/TiO<sub>2</sub>)@rGO-n catalysts.

introduction of supported Pt NPs and wrapping rGO shell, the intensities of PL curves decrease successively, indicating that the ternary nanojunctions can diminish effectively the recombination of photogenerated charges and extend the life of photogenerated electrons, which is beneficial to improve the photocatalytic activity for CO<sub>2</sub> reduction. Among the prepared catalysts, (Pt/TiO<sub>2</sub>)@rGO-2 catalyst exhibits the lowest intensity of PL emission spectra, indicating that the thickness of wrapping rGO sheets can optimize the recombination efficiency of photogenerated charges.

It is well known that the transient photocurrent response induced by the incident light can reflect the enrichment degree of separated charge carriers on the surface of photocatalysts [66]. The higher the photocurrent response is, the larger charge carrier number is [67]. In order to further illustrate the capability of supported Pt NPs and rGO shell for promoting separation efficiency of photoinduced electron-hole pairs in (Pt/TiO<sub>2</sub>)@rGO photocatalysts, the transient photocurrent responses under several on/off UV-vis light irradiation cycles were performed, and the results are showed in Fig. 9. The photocurrent increased immediately when the light irradiation turns on, while it rapidly decreased to zero when the light turns off. The photocurrent density of anatase TiO<sub>2</sub> nanocrystals is higher than that of commercial P25, indicating the relatively high enrichment degree of photogenerated electrons due to the surface heterojunction effect between {001} and {101} facets. Moreover, the transient photocurrent intensities of bi-component Pt/TiO<sub>2</sub> and TiO<sub>2</sub>@rGO-2 catalysts are higher than that of anatase TiO<sub>2</sub> nanocrystals, demonstrating that the photoinduced electrons and holes of Pt/TiO<sub>2</sub> and TiO<sub>2</sub>@rGO catalysts prefer to separate

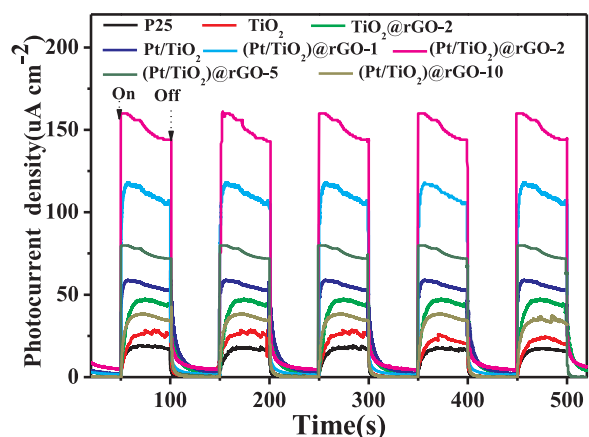


Fig. 9. Transient photocurrent responses of P25, TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, TiO<sub>2</sub>@rGO-2 and (Pt/TiO<sub>2</sub>)@rGO-n catalysts.



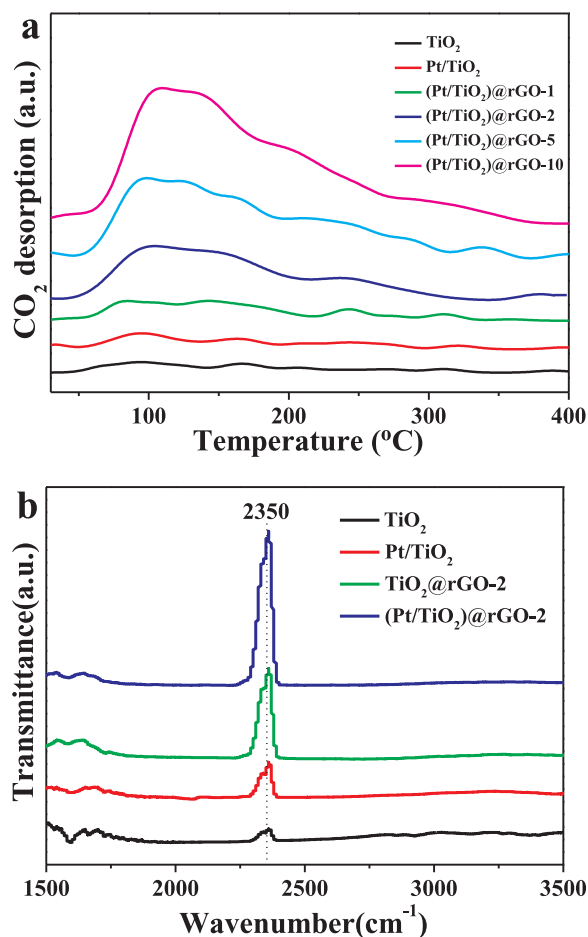


Fig. 10. Temperature-programmed desorption of  $\text{CO}_2$  ( $\text{CO}_2$ -TPD) curves (a) and in-situ  $\text{CO}_2$ -adsorption DRIFTS spectra (b) of  $\text{TiO}_2$ ,  $\text{Pt/TiO}_2$ ,  $\text{TiO}_2$ @rGO-2 and  $(\text{Pt/TiO}_2)$ @rGO-n catalysts.

and transfer to surface rapidly.  $(\text{Pt/TiO}_2)$ @rGO-2 catalyst shows the highest photocurrent density, indicating that it has the most effective separation of the photogenerated charges and the highest surface enrichment degree of photogenerated electrons. The thickness of rGO shell can further optimize the separation efficiency of photogenerated electrons and holes, which is in consistent with the results of PL spectra. During five on/off cycles of light irradiation, all catalysts display a relatively stable photocurrent response, suggesting the good stability of photogenerated charges separation. All the observations with enhanced the separation of photogenerated electrons and holes highlight the excellent performance for photocatalytic reduction of  $\text{CO}_2$  with  $\text{H}_2\text{O}$ .

The adsorption capacity for  $\text{CO}_2$  reactant is also crucial to improve the catalytic activity. Fig. 10 shows the characterizations of  $\text{CO}_2$ -TPD and  $\text{CO}_2$ -adsorption DRIFTS spectra. As shown in Fig. 10a, the catalysts exhibit the desorption peak in the range of 70–180 and 180–350  $^\circ\text{C}$ , which is attributed to the strong physical adsorption and the weak chemical adsorption, respectively. The intensities of  $\text{CO}_2$  desorption curves over  $(\text{Pt/TiO}_2)$ @rGO-n catalysts are higher than those of  $\text{TiO}_2$  and  $\text{Pt/TiO}_2$  catalysts, indicating the strong adsorption capacity for  $\text{CO}_2$  reactant. With the increasing of wrapping rGO shell contents, the intensity of  $\text{CO}_2$  desorption peaks increases remarkably. It indicates that wrapping rGO sheets can improve the adsorption performance of  $\text{CO}_2$ . The  $\text{CO}_2$ -adsorption DRIFTS spectra in Fig. 10b are further confirmed the results of enhanced adsorption capacity of wrapping rGO shell for  $\text{CO}_2$  reactant. The peak at 2350  $\text{cm}^{-1}$  is attributed to the vibration of adsorbed  $\text{CO}_2$  on the surface of catalysts. Among the catalysts, the peak intensity of  $(\text{Pt/TiO}_2)$ @rGO-2 catalyst is highest, and the peak intensities of  $\text{TiO}_2$  and  $\text{Pt/TiO}_2$  catalysts without rGO shells weaken

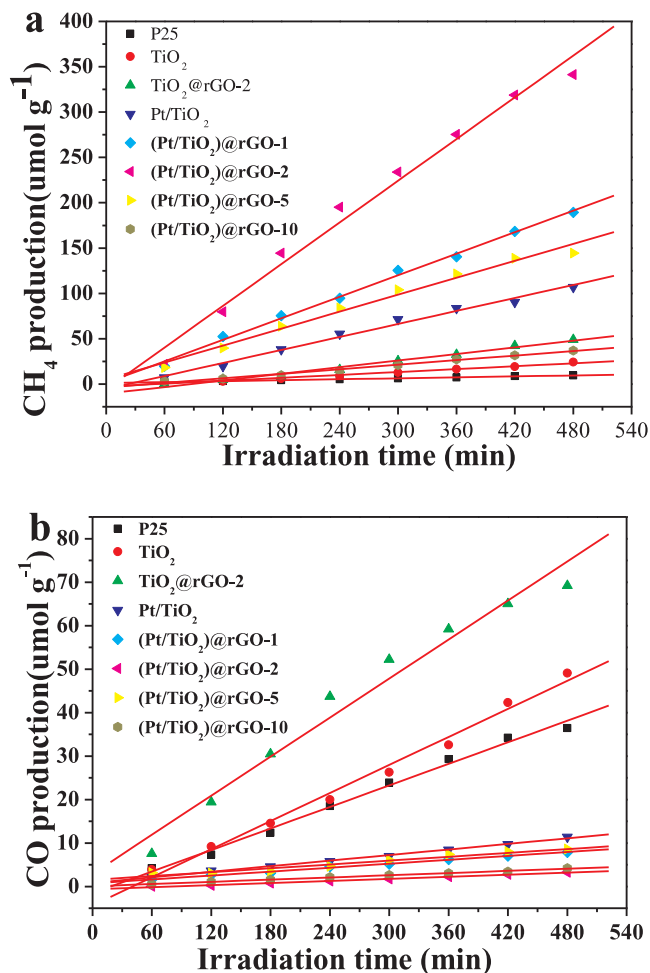


Fig. 11. Evolutions of  $\text{CH}_4$  (a) and  $\text{CO}$  (b) productions for photocatalytic conversion of  $\text{CO}_2$  with  $\text{H}_2\text{O}$  over  $\text{TiO}_2$ ,  $\text{Pt/TiO}_2$ ,  $\text{TiO}_2$ @rGO-2 and  $(\text{Pt/TiO}_2)$ @rGO-n catalysts.

distinctly. It indicates that the wrapping rGO shell can enhance the adsorption capacity of  $\text{CO}_2$  reactant which is benefit for the conversion of  $\text{CO}_2$  to  $\text{CH}_4$ . Based on the results of characterizations,  $(\text{Pt/TiO}_2)$ @rGO-2 catalyst, combined of both optimal photogenerated charges separation efficiency and maximal adsorption capacity for  $\text{CO}_2$  reactant, is promising to exhibit the high photocatalytic activity for  $\text{CO}_2$  reduction with  $\text{H}_2\text{O}$  to hydrocarbon fuels.

### 3.2. Photocatalytic activity for $\text{CO}_2$ reduction under simulated solar irradiation

The photocatalytic reduction of  $\text{CO}_2$  with  $\text{H}_2\text{O}$  was carried out in a gas-closed circulation system with a continuous-flow mode under simulated light irradiation. Commercial P25 was selected as the reference catalyst in photocatalytic  $\text{CO}_2$  reduction. The photocatalytic performances of as-prepared catalysts for  $\text{CO}_2$  reduction with  $\text{H}_2\text{O}$  are shown in Fig. 11 and Table 2. As shown in Fig. 11, the product amounts of  $\text{CH}_4$  and  $\text{CO}$  over anatase  $\text{TiO}_2$  nanocrystals are larger than that of commercial P25. It is attributed to the surface heterojunction between co-exposed {101} and {001} facets in single anatase  $\text{TiO}_2$  nanocrystals for improving the separation of photogenerated charges. The single co-catalysts of wrapping rGO sheets or supported Pt NPs can selectively improve the productive rate of  $\text{CO}$  and  $\text{H}_2$ , respectively.  $\text{TiO}_2$ @rGO-2 catalyst shows highest  $\text{CO}$  formation rate ( $8.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ ), which is ascribed to the enhanced adsorption capacity for  $\text{CO}_2$ .  $\text{Pt/TiO}_2$  catalyst exhibit the highest formation rate of  $\text{H}_2$  ( $72.7 \mu\text{mol g}^{-1} \text{h}^{-1}$ ). It is attributed to the trapping photogenerated electrons of supported Pt NPs

**Table 2**

The formation rates, the selectivity of CO and CH<sub>4</sub> products and the apparent quantum efficiency (AQE) for photocatalytic conversion of CO<sub>2</sub> with H<sub>2</sub>O over TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, TiO<sub>2</sub>@rGO-2 and (Pt/TiO<sub>2</sub>)@rGO-n catalysts.

Sample	Formation rate [ $\mu\text{mol g}^{-1} \text{h}^{-1}$ ] <sup>a</sup>				S <sub>CO</sub> (%) <sup>b</sup>	S <sub>CH<sub>4</sub></sub> (%) <sup>b</sup>	Selectivity for CO <sub>2</sub> reduction (%) <sup>d</sup>	AQE $\Phi_{\text{CH}_4}$ (%) <sup>e</sup>
	CH <sub>4</sub>	CO	H <sub>2</sub>	O <sub>2</sub>				
P25	1.3	1.8	3.8	N.d. <sup>c</sup>	58.1	41.9	64.8	0.06
TiO <sub>2</sub> -001/101	3.4	4.7	5.4	15.5	58.0	42.0	77.2	0.17
Pt/TiO <sub>2</sub>	13.3	1.3	72.7	67.3	7.0	93.0	42.8	0.65
TiO <sub>2</sub> @rGO-2	6.0	8.6	0.8	17.7	58.9	41.1	95.5	0.30
(Pt/TiO <sub>2</sub> )@rGO-1	23.2	0.8	21.1	61.8	3.3	96.7	81.6	1.06
(Pt/TiO <sub>2</sub> )@rGO-2	41.3	0.4	5.6	98.4	0.9	99.1	96.7	1.93
(Pt/TiO <sub>2</sub> )@rGO-5	19.8	1.0	13.7	54.9	4.8	95.2	85.7	0.90
(Pt/TiO <sub>2</sub> )@rGO-10	4.7	0.4	3.7	12.0	7.8	92.2	83.8	0.25

<sup>a</sup>Reaction conditions: photocatalyst, 0.1 g; CO<sub>2</sub> pressure, 0.1 MPa; H<sub>2</sub>O, 2.0 mL; light source, 320–780 nm; irradiation time, 8 h; reaction temperature, 4 °C.

<sup>b</sup> Based on the ratio of [CO] or [CH<sub>4</sub>] amounts to sum ([CO] + [CH<sub>4</sub>]) amounts.

<sup>c</sup> Not determined.

<sup>d</sup> The selectivity was evaluated on an electron basis, equation: Selectivity (%) =  $[2n(\text{CO}) + 8n(\text{CH}_4)]/[2n(\text{CO}) + 8n(\text{CH}_4) + 2n(\text{H}_2)] \times 100\%$ .

<sup>e</sup> The apparent quantum efficiency with irradiation light of 380 nm.

with the lower Fermi energy level. The increased electron density is beneficial to the formation of H<sub>2</sub> during the reaction process of consumption two electrons. Considering that the reduction of H<sub>2</sub>O to H<sub>2</sub> is a competitive reaction with the reduction of CO<sub>2</sub> to CH<sub>4</sub> and CO, we have evaluated the selectivity for CO<sub>2</sub> reduction on an electron basis. It is noted that the photocatalytic selectivity to CO<sub>2</sub> reduction over Pt/TiO<sub>2</sub> catalyst is the lowest, and it increases obviously after wrapped rGO sheets. The selectivities of TiO<sub>2</sub>@rGO and (Pt/TiO<sub>2</sub>)@rGO-n catalysts for CO<sub>2</sub> reduction to CH<sub>4</sub> product are higher than 80%, indicating that wrapping rGO sheets are beneficial to the selective catalytic photoreduction of CO<sub>2</sub> with H<sub>2</sub>O rather than H<sub>2</sub>O reduction to H<sub>2</sub>. Although rGO sheet is a more selective cocatalyst for the reduction of CO<sub>2</sub>, the formation rate of CH<sub>4</sub> over TiO<sub>2</sub>@rGO-2 is lower than that over Pt/TiO<sub>2</sub> catalyst, which may be attributed to the surface low density of photo-generated electrons without Pt NPs.

(Pt/TiO<sub>2</sub>)@rGO-n catalysts exhibited a significantly enhancing photocatalytic activity for CO<sub>2</sub> reduction with H<sub>2</sub>O to CH<sub>4</sub>. Among the as-prepared catalysts, (Pt/TiO<sub>2</sub>)@rGO-2 catalyst shows the highest formation rate of CH<sub>4</sub> ( $41.3 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) and the lowest formation rate of CO ( $0.4 \mu\text{mol g}^{-1} \text{h}^{-1}$ ), its selectivity of CO<sub>2</sub> reduction to CH<sub>4</sub> product is 99.1%. The formation rate of CH<sub>4</sub> over (Pt/TiO<sub>2</sub>)@rGO-2 catalyst has a 31-fold increase in comparison with commercial P25. It shows the noticeable synergistic effect of rGO-Pt-TiO<sub>2</sub> ternary system on enhancing the photocatalytic activity for CO<sub>2</sub> reduction. With increasing of wrapping rGO contents (> 2 wt%), the formation rate of CH<sub>4</sub> decreases remarkably and the selectivity for CO<sub>2</sub> reduction to CO product increases. It is attributed to increased shielding and scattering of photons through excess rGO in the photocatalytic system. Basis on the above results, the role of wrapping rGO shell can be summarized. On the one hand, the advantages of rGO shell are the enhanced adsorption capacity for CO<sub>2</sub> and separation efficiency of photogenerated electron-hole pairs. On the other hand, too much rGO shell can shield the light from reaching the surface of TiO<sub>2</sub> nanocrystals, which results in significant deterioration of photocatalytic performance for CO<sub>2</sub> reduction. Therefore, in order to achieve high efficient photocatalytic CO<sub>2</sub> reduction, the thickness of wrapping rGO shell must be optimized. Among the photocatalysts, (Pt/TiO<sub>2</sub>)@rGO-2 catalyst showed the highest formation rate of CH<sub>4</sub>, indicating that the weight percent (2 wt %) of wrapping rGO sheet is the optimum point between maximum positive and minimum negative effects. In addition, the formation rates of O<sub>2</sub> over the as-prepared catalysts were also investigated. In all the catalysts, (Pt/TiO<sub>2</sub>)@rGO-2 catalyst shows the highest formation rate of O<sub>2</sub> ( $98.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ ) in Table 2, which is higher than the stoichiometric rate according to the calculation of CO<sub>2</sub> reduction products ( $85.6 \mu\text{mol g}^{-1} \text{h}^{-1}$ ). It may be attributed to the formation of other undetected hydrocarbon. Therefore, it is concluded that the moderate

thickness of rGO shell on the surface of Pt/TiO<sub>2</sub>-nanocrystals core is favorable to the photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O and can enhance the formation rate of CH<sub>4</sub>.

The apparent quantum efficiency (AQE) is one of the most important parameters to light-chemical energy conversion. In the photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O reaction, the AQE values for CH<sub>4</sub> product (AQE<sub>CH<sub>4</sub></sub>) over all catalysts were calculated by the equation in part 2.3, and the results are listed in Table 2. The AQE<sub>CH<sub>4</sub></sub> value of anatase TiO<sub>2</sub> nanocrystals (0.17%) is higher than that of P25 (0.06%), indicating that anatase TiO<sub>2</sub> nanocrystal with coexposed {001} and {101} facets is a high efficiency photocatalytic system for CO<sub>2</sub> reduction to CH<sub>4</sub>. The AQE<sub>CH<sub>4</sub></sub> value of Pt/TiO<sub>2</sub> catalyst (0.65%) increases obviously compared with P25 and TiO<sub>2</sub>. Among the (Pt/TiO<sub>2</sub>)@rGO-n catalysts, (Pt/TiO<sub>2</sub>)@rGO-2 catalyst exhibits the largest AQE<sub>CH<sub>4</sub></sub> value (1.93%). It is further confirmed that the suitable thickness of rGO shells on the surface of Pt/TiO<sub>2</sub> nanocrystals is beneficial to improve the utilization efficiency of simulated solar irradiation. Fig. 12 shows the cycle test results of (Pt/TiO<sub>2</sub>)@rGO-2 catalyst for CO<sub>2</sub> reduction. It exhibits excellent stability for photocatalytic CO<sub>2</sub> conversion, i.e., the formation rates of CH<sub>4</sub>, CO and H<sub>2</sub> products have not changed obviously during the ten cycles. And the core-shell structure of (Pt/TiO<sub>2</sub>)@rGO-n catalysts and the particle sizes of supported Pt NPs have not changed based on the results of SEM (Fig. S9a) and TEM (Fig. S9b) images. It indicates that (Pt/TiO<sub>2</sub>)@rGO-n photocatalysts have a strong application potential for photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O.

In addition, a series of background tests were also performed. Under conditions of simulated light irradiation without photocatalysts, any product of CO<sub>2</sub> conversion was not observed. Similarly, any hydrocarbon was not found under condition of without light even using (Pt/

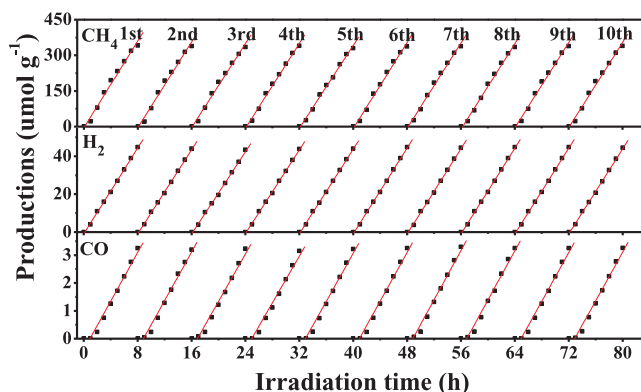


Fig. 12. Stability study on the formation rate of products (CH<sub>4</sub>, CO and H<sub>2</sub>) over (Pt/TiO<sub>2</sub>)@rGO-2 catalyst for ten test cycles.

TiO<sub>2</sub>)@rGO-2 photocatalyst. Using the feed gas of N<sub>2</sub> and H<sub>2</sub>O vapor with (Pt/TiO<sub>2</sub>)@rGO-n catalysts under simulated light irradiation, and again, the carbon-containing products were not detected. In order to verify the sources of carbon and hydrogen in the products of CO and CH<sub>4</sub>, the analyses of <sup>13</sup>C and <sup>2</sup>H(D) isotopic tracing for the products of photocatalytic <sup>13</sup>C-labeled CO<sub>2</sub> reduction with D<sub>2</sub>O over (Pt/TiO<sub>2</sub>)@rGO-2 catalyst were carried out by means of GC–MS after 8 h irradiation (Fig. S10). The peak with *m/z* of 21 can be attributed to <sup>13</sup>CD<sub>4</sub>, and the peak with *m/z* of 29 can be recognized as <sup>13</sup>CO. It indicates that the carbon (C) element in the product of CO and CH<sub>4</sub> comes from CO<sub>2</sub> reactant, and the hydrogen (H) element in the product of CH<sub>4</sub> comes from H<sub>2</sub>O reactant. Therefore, it is asserted that the reactants of CO<sub>2</sub> and H<sub>2</sub>O are only source to photocatalytic products (CO and CH<sub>4</sub>), both photocatalysts and light irradiation must be required for the reaction process of photocatalytic CO<sub>2</sub> reduction with H<sub>2</sub>O.

#### 4. Discussion

It is well known that the photocatalysts for CO<sub>2</sub> reduction must be confirmed to the energy band theory, which is based on the positions of oxidation potentials, conduction band (CB), and valence band (VB). The CB potential (*E*<sub>CB</sub>) of TiO<sub>2</sub> (-0.56 V vs. NHE at pH 7) is more negative than the reduction potentials of *E*<sup>0</sup>(CO<sub>2</sub>/CO) (-0.53 V) and *E*<sup>0</sup>(CO<sub>2</sub>/CH<sub>4</sub>) (-0.24 V), so the reduction reaction is theoretically feasible. Although the *E*<sup>0</sup>(CO<sub>2</sub>/CH<sub>4</sub>) is less negative than *E*<sup>0</sup>(CO<sub>2</sub>/CO), but eight electrons are required to produce CH<sub>4</sub> rather than only two electrons for CO product [68]. Thus, the CO product is possible to be priority owing to the paucity of photogenerated electrons. But if the protons and electrons are sufficiently afforded during the photocatalytic process, CH<sub>4</sub> should be the major reduction product. Moreover, the basic process of photocatalytic CO<sub>2</sub> reduction can be summarized into three steps: 1) formation of photogenerated carriers (electron-hole pairs) by a band-gap excitation, 2) separation and transportation of the charge carriers, 3) reduction of water and carbon dioxide adsorbed on the surface of catalysts by the photogenerated electrons. Thus, the introduction of co-catalyst should be beneficial to improve the charge separation, facilitate the CO<sub>2</sub> adsorption and activation, and increase the catalytic active sites for the reduction process. Above all, the formation rate and selectivity of CH<sub>4</sub> products are dependent on the enrichment degree of electrons and reactants on the surface of photocatalysts, which is strongly related to the nanostructure and the surface property of photocatalysts.

Based on the results of photocatalytic CO<sub>2</sub> conversion with H<sub>2</sub>O in Table 2, (Pt/TiO<sub>2</sub>)@rGO-n catalysts exhibited super catalytic performances. The enhanced photocatalytic activity for CO<sub>2</sub> conversion with

H<sub>2</sub>O can be isolated from light-harvesting, CO<sub>2</sub> adsorption and activation, and charge-separation functions of the photocatalysts. For improving the light-harvesting efficiency, the co-catalysts of supported Pt NPs and wrapping rGO sheets with the electronic coupling between  $\pi$  states of rGO and CB states of TiO<sub>2</sub> can effectively extend the spectral response from UV to visible region (Fig. 7). Based on comparison of the UV–vis DRS results between TiO<sub>2</sub> and (Pt/TiO<sub>2</sub>)@rGO-2 catalysts, it is noted that the supported rGO sheets can further improve the absorption for visible light due to the electronic coupling between  $\pi$  states of rGO and conduction band states of TiO<sub>2</sub>. For enhancing CO<sub>2</sub> adsorption capacity, wrapping rGO sheets play the main role owing to their identical nonpolar property and abundant  $\pi$  electron cloud supported by the results of CO<sub>2</sub>-TPD and CO<sub>2</sub>-adsorption DRIFTS spectra (Fig. 10).

For effective separation efficiency of photogenerated charges, the rapidly interfacial charge transfers from the surface heterojunction of {101} and {001} facets to Pt NPs and subsequent to rGO shell. Primarily, anatase TiO<sub>2</sub> nanocrystals are excited to produce electron-hole pairs by absorbed photons. The coexposed {101} and {001} facets of anatase TiO<sub>2</sub> nanocrystals can form a surface heterojunction, which is beneficial to effective separation of photogenerated electrons and holes. And then photogenerated electrons in the CB of TiO<sub>2</sub> transfer to supported Pt NPs. Combined the results of XPS (Fig. 5), PL (Fig. 8) and transient photocurrent (Fig. 9), the increasing of surface Pt<sup>δ+</sup> species has strong capacity to capture the electron from CB of TiO<sub>2</sub>. The supported Pt NPs in (Pt/TiO<sub>2</sub>)@rGO-n catalysts are used as an accumulator and sensor for electron transfer in TiO<sub>2</sub>-Pt-rGO ternary system. And the photogenerated electrons can further transfer to rGO rather than stay in supported Pt NPs because of the strong electron withdrawing capacity of wrapping rGO shell, which can be illuminated by the increasing of Pt<sup>δ+</sup> species after introduction of rGO sheets. Thus, it occurs the vectorial electron transfer from TiO<sub>2</sub> to Pt NPs and even to rGO shell (TiO<sub>2</sub> → Pt → rGO). Finally, the photogenerated electrons are enriched on the tiny surface region of wrapping rGO shell, and subsequently react with the adsorbed CO<sub>2</sub> to CH<sub>4</sub>. In order to verify the vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO, the experiment of Ag photodeposition on the surface of (Pt/TiO<sub>2</sub>)@rGO-2 catalyst was carried out by irradiation with same light source of CO<sub>2</sub> reduction test for 30 min, and the results are shown in Fig. S11. The TEM images of Ag photodeposition over (Pt/TiO<sub>2</sub>)@rGO-2 catalyst. Ag NPs with large sizes are almost deposited selectively on the surface of wrapping rGO shell and Ag/(Pt/TiO<sub>2</sub>)@rGO structure is formed. It indicates that the surface electron-rich region of wrapping RGO sheets is the active site of (Pt/TiO<sub>2</sub>)@rGO-2 catalysts, which also proves the vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO.

Based on the discussion above, the mechanism for the

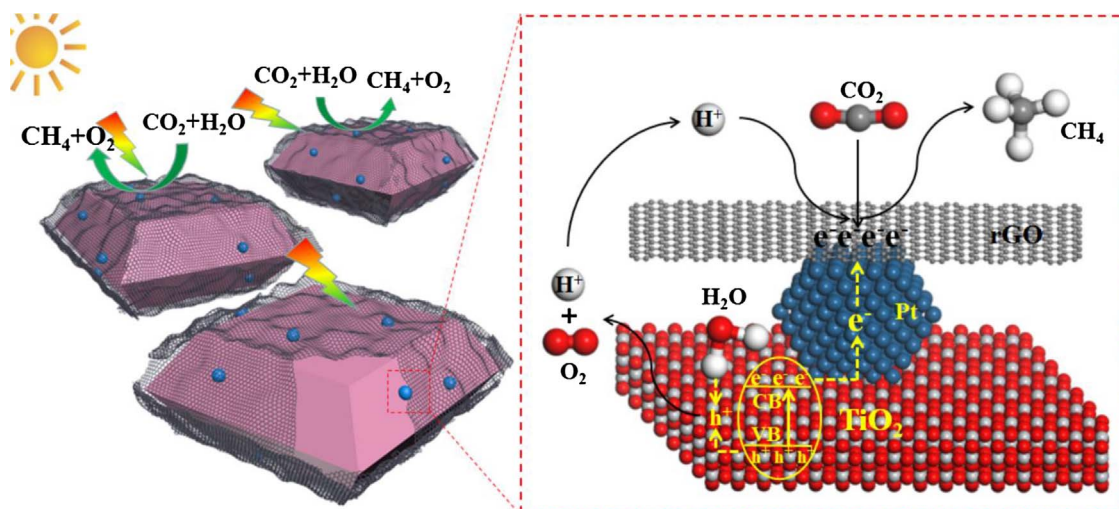


Fig. 13. Schematic of the mechanism for CO<sub>2</sub> photoreduction with H<sub>2</sub>O to CH<sub>4</sub> over (Pt/TiO<sub>2</sub>)@rGO-n catalysts.



photoreduction CO<sub>2</sub> with H<sub>2</sub>O over (Pt/TiO<sub>2</sub>)/rGO catalysts is proposed and vividly shown in Fig. 13. In the rGO-Pt-TiO<sub>2</sub> ternary composites, anatase TiO<sub>2</sub> nanocrystals are the fountain of photogenerated electrons, and the coexposed {101} and {001} facets undertake a spade work for separation of electrons and holes. Supported Pt NPs act a key role to gather photogenerated electrons from the CB of anatase TiO<sub>2</sub> nanocrystal. And photogenerated electrons are enrichment on the tiny region of wrapping rGO shell via the vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO. Ultimately, photogenerated electrons form an enriched region on the wrapping rGO shell, where CO<sub>2</sub> is reduced to CH<sub>4</sub> by the photogenerated electrons and H<sup>+</sup>. The holes left on the surface of TiO<sub>2</sub> nanocrystals can react with H<sub>2</sub>O to O<sub>2</sub> accompanied by the generating of hydrogen ion for the consumption of CO<sub>2</sub> reduction. Meanwhile, the identical nonpolar property and abundant  $\pi$  electron cloud are conducive to the adsorption of CO<sub>2</sub>. This mechanism can ideally explain that the suitable thickness of rGO shells on the surface of Pt/TiO<sub>2</sub> is beneficial to CO<sub>2</sub> reduction and can enhance the formation rate of CH<sub>4</sub> except the influence from absorbance of rGO shells. The formation of RGO shells was incomplete with less content of rGO. And as mentioned earlier, too thick rGO shells can shield the light from reaching the surface of the TiO<sub>2</sub> photocatalyst and decrease the yield of photogenerated charges. There is a balance between the maximum positive and the minimum negative effects. Thus, the optimized rGO-Pt-TiO<sub>2</sub> ternary composites are beneficial to the multi-electron process of photocatalytic CO<sub>2</sub> conversion, and the unique electron collecting and transfer capabilities of rGO shell promote the selective production of CH<sub>4</sub> in photocatalytic CO<sub>2</sub> conversion. In other words, the vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO over the ternary composites system is beneficial to the separation of photogenerated electrons and holes, which can increase the formation rates and selectivity of CH<sub>4</sub> for CO<sub>2</sub> reduction. Therefore, (Pt/TiO<sub>2</sub>)/rGO catalysts, which takes all advantages of the high separation efficiency of photogenerated electrons and holes and the enhanced adsorption and activation capacities for CO<sub>2</sub> reactant, exhibited super photocatalytic performance for selective CO<sub>2</sub> conversion to CH<sub>4</sub> under the simulated solar irradiation.

## 5. Conclusions

We demonstrated a strategy to fabricate the novel core-shell-structured photocatalysts of Pt/TiO<sub>2</sub> nanocrystals wrapped by rGO sheets. Anatase TiO<sub>2</sub> nanocrystals with coexposed {001} and {101} facets can enhance the photogenerated charges separation efficiency preliminarily. Supported Pt NPs on the surface of TiO<sub>2</sub> nanocrystals are crucial to transfer and gather of photogenerated electrons for CO<sub>2</sub> conversion. The wrapping rGO sheets as an efficient electron acceptor and transporter are not only beneficial to enhance the enrichment of photogenerated electrons, but also their surface intrinsic hydroxyl and extended  $\pi$  bond are beneficial to enhance the adsorption and activation for CO<sub>2</sub> reactant. The rGO(shell)-Pt(medium)-TiO<sub>2</sub>(core) ternary composites can promote the vectorial electron transfer of TiO<sub>2</sub> → Pt → rGO and enhance photogenerated charges separation. (Pt/TiO<sub>2</sub>)/rGO-2 catalyst, which takes both advantages of the enhancing adsorption capacity of CO<sub>2</sub> reactants and the high separation efficiency of photogenerated electrons and holes, exhibited highest photocatalytic activity and selectivity for CO<sub>2</sub> conversion with H<sub>2</sub>O to CH<sub>4</sub> under simulated solar irradiation, i.e., its formation rate of CH<sub>4</sub> (41.3  $\mu\text{mol g}^{-1} \text{h}^{-1}$ ) is about 31-fold of commercial P25 and the selectivity of CO<sub>2</sub> conversion to CH<sub>4</sub> product is closely to 100%. The innovative design and fabrication of (Pt/TiO<sub>2</sub>)/rGO photocatalysts, based on the aim of improving photogenerated charges separation and CO<sub>2</sub> adsorption capacity, are expected to be a new heuristic on the development of selectively photocatalytic CO<sub>2</sub> conversion to CH<sub>4</sub>.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcatb.2017.12.071.

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